Supporting Information

Notable Formation of a Cubic Phase from Small Bent-angle Molecules Based on the 1,7-Naphthalene Central Core and Alkylthio Tails

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Scheme S1 Synthesize route to N(1,7)-S-n compound
**Synthesis and analytical data**

The target bent-shaped molecules were synthesized by following the methods in our previous paper. The synthetic routes were illustrated in Scheme S1. All reagents including bis(p-hydroxyphenyl)methane were purchased from TCI (Tokyo Kasei kogyo Co, Ltd) and used without further purification. Solvents were purified by normal procedures and handled under a moisture-free atmosphere. $^1$H-NMR and $^{13}$C-NMR spectra were recorded on a JEOL FT-NMR AL400 (400 MHz) spectrometer using CDCl$_3$ as an internal standard. Elemental analysis was determined by CHN corder MT-6.

**Synthesis of dialdehydes 3**

To a solution of 1,7-dihydroxynaphthalene 1 (1.00 g, 6.24 mmol) in CH$_2$Cl$_2$ (100 ml) was added 1,3-dicyclohexylcarbodiimide (DCC) (3.22 g, 15.60 mmol), 4-dimethylaminopyridine (DMAP) (catalyst amount), and 4-formylbenzoic acid 2 (2.06 g, 13.72 mmol). The mixture was stirred at room temperature for three days. After filtration to remove precipitated materials, the filtrate was chromatographed on silica gel (CH$_2$Cl$_2$) and then recrystallized from dichloromethane/ethanol to isolate 3 (1.35 g, 51%) as a white solid. $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ 7.42-8.07 (m, 6H), 8.37 (d, J=8.4 Hz, 4H), 8.48 (d, J=8.4 Hz, 4H), 10.14 (s, 1H), 10.16 (s, 1H).

**Synthesis of N-(4-dodecylsulfanylphenyl)acetamide 5-22**

A mixture of 4-acetamidobenzenethiol 4 (2.60 g, 15.5 mmol), 1-bromodocosane (7.32 g, 18.8 mmol) and potassium carbonate (6.41 g, 46.5 mmol) in acetone (100 ml) was heated under reflux 16h (For 1-Bromotetracosane, 1-Bromohexacosane and 1-Bromotriacosane, they were prepared by bromination of n-alcohol with hydrogen bromide). To this solution was added water (50 ml) and the produce was extracted with diethyl ether (30 ml × 3). The combined organic layers were dried (MgSO$_4$),
concentrated and recrystallized from ethanol to give 5-22 (4.4 g, 60%) as a white solid. $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ 0.88 (t, J=6.6 Hz, 3H), 1.25-1.61 (m, 40H), 2.17 (s, 3H), 2.86 (t, J=7.4 Hz, 2H), 7.05 (br s, NH), 7.30 (d, J=8.4 Hz, 2H), 7.42 (d, J=8.3 Hz, 2H).

For 5-24, $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ 0.88 (t, J=6.7 Hz, 3H), 1.26-1.62 (m, 44H), 2.17 (s, 3H), 2.86 (t, J=7.3 Hz, 2H), 7.05 (br s, NH), 7.30 (d, J=8.5 Hz, 2H), 7.42 (d, J=8.1 Hz, 2H).

For 5-26, $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ 0.88 (t, J=6.7 Hz, 3H), 1.25-1.61 (m, 48H), 2.18 (s, 3H), 2.86 (t, J=7.4 Hz, 2H), 7.06 (br s, NH), 7.30 (d, J=8.5 Hz, 2H), 7.42 (d, J=8.3 Hz, 2H).

For 5-30, $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ 0.88 (t, J=6.1 Hz, 3H), 1.25-1.61 (m, 56H), 2.17 (s, 3H), 2.86 (t, J=6.1 Hz, 2H), 7.06 (br s, NH), 7.30 (d, J=8.3 Hz, 2H), 7.41 (d, J=8.5 Hz, 2H).

**Synthesis of 4-dodecylsulfanylphenylamine 6-22**

An ethanol (100 ml) solution of 5 (4.4 g, 9.30 mmol) and a catalytic amount of concentrated HCl was stirred at 70°C. After 1 day, the solvent was evaporated *in vacuo*; saturated NaHCO$_3$ (50 ml) was added to the residue. The mixture was filtered and dried, then give 6 (3.91 g, 97%). $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ 0.86 (t, J=6.8 Hz, 3H), 1.25-1.52 (m, 20 H), 2.72 (t, J=7.2 Hz, 2H), 3.20 (br s, NH$_2$), 6.63 (d, J=8.5 Hz, 2H), 7.10 (d, J=8.3 Hz, 2H).

For 6-24, $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ 0.86 (t, J=6.8 Hz, 3H), 1.25-1.50 (m, 44 H), 2.68 (t, J=7.1 Hz, 2H), 3.01 (br s, NH$_2$), 6.53 (d, J=8.5 Hz, 2H), 7.06 (d, J=8.8 Hz, 2H).

For 6-26, $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ 0.87 (t, J=6.8 Hz, 3H), 1.25-1.50 (m, 48 H), 2.75 (t, J=7.3 Hz, 2H), 3.10 (br s, NH$_2$), 6.60 (d, J=8.8 Hz, 2H), 7.10 (d, J=8.8 Hz, 2H).
For 6-30, $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ 0.88 (t, J=6.6 Hz, 3H), 1.20-1.49 (m, 36 H), 2.70 (t, J=7.3 Hz, 2H), 4.88 (br s, NH$_2$), 6.54 (d, J=8.8 Hz, 2H), 7.06 (d, J=8.3 Hz, 2H).

**Synthesis of 1,7-naphthalene bis[4-(4-dodecylsulfanylphenyliminomethyl)benzoate].**

A solution of 6 (0.31 g, 1.08 mmol) and dialdehyde 3 (0.20 g, 0.47 mmol) in chloroform (25 ml) was heated under reflux for 3 hr. The reaction mixture was concentrated and recrystallized from chloroform/ethanol twice to give a yellow crystal of the target compound, N(1,7)-S-22 (0.33 g, 72%).

The NMR and Elemental analysis data are shown;

$^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ 0.87 (t, J=6.8 Hz, 6H), 1.28-1.70 (m, 80H), 2.94 (t, J=7.3 Hz, 4H), 7.22-8.08 (m, 18H), 8.30 (d, J=8.3 Hz, 2H), 8.41 (d, J=8.5 Hz, 2H), 8.55 (s, 1H), 8.57 (s, 1H).

$^{13}$C-NMR (400 MHz, CDCl$_3$) $\delta$ 15.36, 23.96, 30.13, 30.47, 30.49, 30.63, 30.79, 30.87, 30.89, 30.91, 30.92, 30.93, 30.95, 30.96, 30.97, 30.99, 31.10, 31.11, 31.13, 31.15, 33.20, 35.31, 120.37, 122.87, 122.89, 123.39, 126.79, 128.88, 130.03, 130.19, 131.13, 131.15, 131.17, 131.92, 132.05, 136.99, 146.35, 150.35, 150.64, 159.30, 159.33, 165.99.

Elemental analysis: calculated for C$_{82}$H$_{114}$N$_2$O$_4$S$_2$ C 78.42, H 9.15, N 2.23, O 5.10, S 5.11; found, C 78.37, H 9.17, N 2.25, O(+ S) 10.21.

Other target compounds, N(1,7)-S-24, N(1,7)-S-26 and N(1,7)-S-30 were similarly prepared in 52 %, 44 % and 42 % yields, respectively.

The NMR and Elemental analysis data are shown; For N(1,7)-S24, $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ 0.88 (t, J=7.0 Hz, 6H), 1.25-1.66 (m, 88H), 2.94 (t, J=7.1 Hz, 4H), 7.20-8.09 (m, 18H), 8.30 (d, J=8.3 Hz, 2H), 8.42 (d, J=8.5 Hz, 2H), 8.55 (s, 1H), 8.58 (s, 1H).

$^{13}$C-NMR (400 MHz, CDCl$_3$) $\delta$ 15.40, 24.03, 30.18, 30.45, 30.52, 30.70, 30.85, 30.88, 30.92, 30.94, 30.99, 31.03, 33.26, 35.21, 122.75, 122.94, 122.95, 124.06, 124.73, 130.08, 130.23, 131.04, 131.99, 132.11, 142.04, 150.26, 170.25

Elemental analysis: calculated for C$_{86}$H$_{122}$N$_2$O$_4$S$_2$ C 78.73, H 9.37, N 2.14, O 4.88, S 4.89; found, C 78.70, H 9.41, N 2.17, O(+ S) 9.72.
For N(1,7)-S26, $^1$H-NMR 0.88 (t, J=6.6 Hz, 6H), 1.25-1.70 (m, 96H), 2.94 (t, J=7.4 Hz, 4H), 7.20-8.09 (m, 18H), 8.30 (d, J=8.3 Hz, 2H), 8.42 (d, J=8.5 Hz, 2H), 8.55 (s, 1H), 8.58 (s, 1H).

$^{13}$C-NMR (400 MHz, CDCl3) $\delta$ 15.46, 24.03, 30.18, 30.44, 30.52, 30.70, 30.85, 30.87, 30.93, 30.96, 31.00, 31.04, 33.26, 35.21, 122.94, 122.95, 128.87, 130.08, 130.23, 131.03, 131.24, 131.99, 132.11, 136.99, 147.86, 150.26, 159.44

Elemental analysis: calculated for C$_{90}$H$_{130}$N$_2$O$_4$S$_2$ C 79.01, H 9.58, N 2.05, O 4.68, S 4.69; found, C 78.95, H 9.62, N 2.10, O(+ S) 9.33.

For N(1,7)-S30, $^1$H-NMR 0.88 (t, J=6.8 Hz, 6H), 1.25-1.70 (m, 112H), 2.94 (t, J=7.3 Hz, 4H), 7.20-8.09 (m, 18H), 8.30 (d, J=8.1 Hz, 2H), 8.42 (d, J=8.5 Hz, 2H), 8.55 (s, 1H), 8.58 (s, 1H).

$^{13}$C-NMR (400 MHz, CDCl3) $\delta$ 15.46, 30.17, 30.45, 30.85, 30.93, 31.00, 31.04, 31.07, 33.26, 35.21, 122.94, 128.25, 130.23, 131.03, 148.73

Elemental analysis: calculated for C$_{98}$H$_{146}$N$_2$O$_4$S$_2$ C 79.51, H 9.94, N 1.89, O 4.32, S 4.33; found, C 79.23, H 9.94, N 1.91, O(+ S) 8.92.
FIGURE CAPTION

Fig. S1 Polarization reversal current in the Colₕ phase of N(1,7)-S-22 upon the application of the triangular wave (Temperature: 130 °C, Voltage: 120 Vpp, Frequency: 200 Hz, and Cell gap: 2.4 µm). A single reversal current peak can be clearly detected in the half period of the triangular wave field.

Fig. S2 Temperature dependence of the spontaneous polarization observed in N(1,7)-S-22 (Voltage: 120 Vpp, Frequency: 200 Hz, and Cell gap: 2.4 µm). The solid curve is calculated according to the equation of $P_s = P_{s0} (1 - T/T_{tr})^\beta$ with $P_{s0} = 628 \text{nC} \cdot \text{cm}^2$, $\beta = 0.37$, and $T_{tr} = 141 \text{ K}$.
Figure S1
Figure S2